THE HYDRATION OF SO_2: AN *AB INITIO* INVESTIGATION

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Ab initio quantum chemical techniques have been used to investigate weakly bound complexes of H_2O and SO_2. An energy gradient program was used to locate stable structures for the H_2O-SO_2 complexes and SCF calculations were carried out to determine the binding energies of complexes with multiple water molecules. A 4-31G basis set was used for most potential energy searches. More accurate basis sets including a generally contracted basis set with d orbitals on the sulfur were used for geometry and binding energy verification. For single water complexes five different stable geometries were located, with binding energies between 4 and 11 Kcal mol^{-1} suggesting a binding shell for H_2O around SO_2 and a mechanism for the formation of an SO_2-containing water droplet. Very little charge transfer between SO_2 and H_2O was present. Addition of more than one H_2O was found to be energetically favorable although the addition of the fourth water in certain geometries did not increase the stability of the complex. An alternative mechanism for the tropospheric, gas phase production of acid rain is suggested.

Introduction

The oxidation of SO_2 is an important chemical process. The phenomenon of "acid rain" involves the oxidation of sulfur containing species including SO_2 to form SO_3. Hydration is involved to give H_2SO_4 which in turn is ultimately precipitated as sulfates.[1] The influence which water plays on the kinetics of oxidation is less clear. However, Rees noted a 4.7×10^3 fold increase in the rate of photo oxidation of SO_2 in the 283% relatively humidity of a Wilson cloud chamber over that in the absence of water.[2] SO_2 may also act as the nucleation center for aerosol formation. The exact mechanism of such a process, should it exist, is not known.

The stability of a complex of SO_2 and H_2O was first suggested by Phillips on the basis of results of semiempirical calculations.[3] Holland and Castleman using CNDO/2 calculations suggested that an $SO_2 \cdot H_2O$ adduct should be stable in the gas phase and reported a binding energy of 145 mH and a large dipole moment.[4]

Evidence for the existence of $H_2O \cdot SO_2$ produced from the photolysis of H_2S in solid O_2 at 15K by ultraviolet light is presented by Tso and Lee who conducted an FTIR study of the photolysis mixture.[5] Identification was based on shifted vibrational bands of SO_2 and H_2O.

The stability of SO_2-water complexes has also been suggested from molecular beam measurements, and electric deflection experiments indicate a large dipole moment for the complex.[6]

Although there have been no ab initio calculations of the $SO_2 \cdot H_2O$ complex there are calculations for related complexes. Ab initio calculations on $SO_2 \cdot NH_3$[7] and $SO_2 \cdot HF$[8] show stable complexes for a variety of geometries. An important pair of calculations was done on the closely related complex $H_2 \cdot SO_3$ and its rearrangement to H_2SO_4. A semiempirical CNDO/2 calculation by Holland and Castleman[9] has been followed by a recent ab initio calculation by

Chen and Plummer.[10]

In an effort to shed some light on a possible role of H_2O in the oxidation of SO_2 and elucidate the structure and energetics of formation of water complexes of SO_2, we have undertaken an ab initio study.

$SO_2 \cdot (H_2O)_1$

To explore the possibility of bound conformations of $H_2O \cdot SO_2$ an SCF energy gradient program[11] was used to locate stable structures for the complex. The 4-31G basis set was used for the initial potential energy searches. The minimum energy geometry was established when the largest energy gradient at any atom was reduced to the order of 1m Hartree per Bohr.

Five distinct conformations of the single water complex were found to be bound. These are shown in Figure 1. The total energies for the complexes and the molecular fragments as well as the binding energies are given in Table 1. The minimum energy geometry information is given in Table 2.

Conformations III and IV bear the closest relationship to classical hydrogen bonded structures, having respectively, one and two such bonds, and no significant binding interaction between the water oxygen and the sulfur atom. Conformation I, the most weakly bound, is at the opposite end of the scale with no hydrogen bonding, but has a favorable dipole interaction and a loose coordination between the water oxygen and the sulfur atom. Conformations II and V exhibit intermediate characteristics with both hydrogen bonding and O-S coordination. Except for the interplanar angle between the two moieties, conformation V, the most strongly bound, exhibits the energetically most favorable alignment of the fragment dipoles.

Hydrogen transfer with subsequent charge and structural relaxation from either conformation II or V would lead to the presumed structure of sulfurous acid. The coordination of the water oxygen and sulfur atom in conformations I, II, and V could also facilitate other reactions leading to oxidation of

SO_2.

In conformation III the out-of-plane angle of rotation of the nonhydrogen-bonded OH is very soft energetically and no angle is favored by more than a few tenths of a milliHartree. Conformation V was suggested by the results of a semiempirical calculation[4] but the minimum energy geometry result here indicates a preference for a cis arrangement rather than the trans arrangement of the semiempirical calculation.

To examine the effect of basis set size on the binding energy and geometry two additional SCF energy gradient calculations were performed on conformation V. In the first calculation a double zeta basis set was employed. The primitive basis set, a Huzinaga sulfur (12s/8p), oxygen (9s/5p), hydrogen (4s) set, was segmentally contracted.[12,13] A Dunning contraction of the hydrogen and oxygen orbitals, O(9s/5p)/<6111/41>, H(4s)/<3 1>, and a McLean contraction of the sulfur orbitals, S(12s/8p)/<62211/621>, were chosen.[14,15] The binding energy decreased by 3.0 mH, a rough measure of the superposition error in the poorer basis set. In the second calculation a set of sulfur 3d orbitals ($\zeta_{3d} = 0.6$) was added to this basis set. The polarization functions reduced the SO_2 bond angle, decreased the SO_2 dipole moment, and lowered the binding energy of the complex by an additional 2.4 mH. The results of these two calculations are given in Tables 1 and 2.

$SO_2 \cdot (H_2O)_n$

Selected two-water complexes were studied using the energy gradient program with the 4-31G basis set. The conformations are shown in Figure 2. Conformations VI and VII are mirror image doublings of conformations I and V, respectively.

The interatomic distances did not change significantly in going to the two-water complexes. The energies are given in Table 1. In both cases the binding energy of the two-water complexes are a little less than twice the binding energies of the one-water complexes indicating relatively little interaction between the water molecules and almost independent addition of the second water molecule.

In order to examine the energetics of adding multiple waters to SO_2 with the double zeta plus sulfur d orbital basis set, SCF calculations were run using a generally contracted basis set at fixed geometries predicted by the earlier gradient results. The primitive basis set was again the Huzinaga sulfur (12s/8p), oxygen (9s/5p), hydrogen (4s) set generally contracted to <4s/3p>, <3s/2p>, and <2s>, respectively.[12,13,16] This set was augmented by a single set of 3d functions (ζ_{3d} = 0.6) on the sulfur atom. This basis set was similar to the previous double zeta plus d set and the binding energy of conformation V obtained with this new basis set differed by only 0.2 mH from the previous result.

The multiple-water complexes studied are shown in Figure 2. The total energies and binding energies are given in Table 1. Conformation I with this basis set produces a binding energy which is 72% of the binding energy derived from the earlier 4-31G calculation. This reduction in binding energy is virtually identical to that obtained for conformation V. The multiple-water complexes $SO_2\ (H_2O)_n$ with n = 3 and 4 differ by only a few mH from the sum of the binding energies of the separate bound pairs. This assumes that the energies of the conformations II and IV (which were not calculated with the larger basis) can be approximated by taking 70% of the binding energy obtained with the 4-31G basis set. The binding energy of the five-water complex is, however, significantly less than the sum of the binding energies of the separate bound-pairs.

Further improvements in the basis set and the inclusion of correlation effects might be expected to increase the predicted binding energies by as much as 20 percent.[17,18]

The implications of the additivity of the binding energies supports the notion that the bonding interaction is nearly purely electrostatic. Only when the waters were close enough to interact with each other, as in the five-water complex, did the binding energy fall significantly below the sum of the binding energies of the separate bound pairs. An interesting corollary to the approximate additivity of the binding energies occurred in the three water complex, conformation VIII, which was slightly more stable than predicted from the binding energy additivities perhaps due to a favorable alignment of the water dipoles. These results suggest that, the binding energy of some multiple water complexes which could be modeled by superposition of smaller complexes, but which have not been investigated here, would deviate significantly from additivity due to water-water interactions.

Although a Morakuma component analysis[19] of the energy components of the H_2O - SO_2 interaction was not made, the results obtained here suggest that the analysis would follow that for the $NH_3 \cdot SO_2$ complex[7] as discussed by Kollman.[20] Mulliken population analyses[21] of the results of SCF calculations on the H_2O-SO_2 complex using the best basis set show a small charge transfer resulting in a small negative charge on the SO_2. See Table 1. With the 4-31G basis set the charge transfer was about fifty percent larger, a consequence of basis set superposition error. The 4-31G basis set calculation for conformation IV produced the unique result of a charge transfer in the opposite direction from all the other results. Since the charge transfer and polarization affects are small, the minimum energy geometry is determined by a balance of the electrostatic energy and the exchange repulsion energy. However, unlike the $NH_3 \cdot SO_2$ complex, the minimum energy orientation for the

H_2O and SO_2 fragments in conformation V is closer to that predicted solely from consideration of the dipole-dipole interaction.

The H-bonded complex, conformation III, has a binding energy (4.7 Kcal) which is virtually the same as that obtained for the HF · SO_2 complex (5Kcal).[8] The minimum energy complex, conformation V, has a binding energy (10.9 Kcal) very close to that obtained for the NH_3 · SO_2 complex (9.3 Kcal).[7] It should be noted that inclusion of d orbitals in the sulfur basis set reduced the binding energy of NH_3 · SO_2 from 10.4 Kcal to 9.3 Kcal, an effect that was also observed in the H_2O · SO_2 calculations. The CNDO/2 results of Castleman gave a much larger binding energy (98.3 Kcal) and a different minimum energy geometry.[4]

In the analysis of his molecular beam electric deflection results Castleman, remarks on the existence of species with large dipole moments that he attributes to H_2O · SO_2 complexes.[6] The dipole moments for some of the complexes were calculated in this study and are reported in Table 2. These values are all overestimated, particularly those from calculations which did not include sulfur d orbitals in the basis set.

The gradient SCF program can also be used to produce force constants and fundamental frequencies for vibrational modes. However, the equilibrium geometries were not converged to sufficient accuracy to enable predicting the sizes and signs of the frequency shifts of SO_2 and H_2O vibrations upon complexation. Better convergence would allow comparison with the experimental IR spectroscopic results of Tso and Lee who claim to have evidence for the existence of the H_2O · SO_2 complex.[5]

There are two implications from these results for acid rain chemistry. The most widely accepted mechanism for the tropospheric, gas phase production of H_2SO_4 is as follows:

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \quad (1)$$

$$O(^1D) + H_2O \longrightarrow 2HO \quad (2)$$

$$HO + SO_2 + M \longrightarrow HOSO_2 + M^* \quad (3)$$

$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3 \quad (4)$$

$$SO_3 + H_2O + M \longrightarrow H_2SO_4 + M^* \quad (5)$$

This ab initio study shows that an $H_2O \cdot SO_2$ complex is predicted to and therefore an alternative to steps (2) and (3) above is suggested:

$$H_2O + SO_2 + M \rightleftarrows H_2O\ SO_2 + M^* \quad (2')$$

$$O(^1D) + H_2O\ SO_2 \longrightarrow OH + HOSO_2 \quad (3')$$

Thus the reaction which produces the important intermediate $HOSO_2$ be bimolecular rather than termolecular. An estimate of the concentration c complex and comparison of the activation energies from the alternative needed to decide between them. Other (speculative) possibilities wc include:

$$O(^3P) + H_2O\ SO_2 \longrightarrow OH + HOSO_2 \quad (3'')$$

$$O(^1D) + SO_2\ (H_2O)_2 \longrightarrow H_2SO_4 + H_2O \quad (3''')$$

$$O(^3P) + SO_2\ (H_2O)_2 \longrightarrow H_2SO_4 + H_2O \quad (3'^{v})$$

The second implication for acid rain chemistry comes from the results of the multiple-water complexes. There appears to be a shell of bonding sites for H_2O around a central SO_2. This suggests the formation of a nucleation center with additional waters outside the initial sphere added in a typical H-bonded fashion to waters already in the complex. The energetics are favorable but a discussion of the position of equilibrium would have to include an evaluation of the entropy changes for the process. The formation of an SO_2-containing droplet would allow heterogeneous chemistry to proceed.

In summary, an energy gradient program was used to lo structures for $H_2O \cdot SO_2$ complexes and SCF calculations were car determine the binding energies of complexes with multiple water mo 4-31G basis set was used for most potential energy searches. Mor basis sets including a generally contracted basis set with d orbita sulfur atom were used for geometry and binding energy verification. water complexes five different stable geometries were located, with energies between 4 and 11 Kcal mol^{-1} suggesting a binding shell for H_2O SO_2. Very little charge transfer between SO_2 and H_2O was present. Ad of more than one H_2O was found to be energetically favorable and approxim additive up to four added waters. An alternative mechanism for tropospheric, gas phase production of acid rain is suggested. A process the formation of an SO_2 containing water droplet is advanced.

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Table 1. SCF total energies (Hartrees), binding energies (Kcal mol^{-1}) in parentheses, and total charge on SO_2 of SO_2 $(H_2O)_n$ complexes.

	Geometry Optimized			Geometry Fixed	
H_2O	-75.9086	-76.0110	-76.0110	-76.0121	-
SO_2	-546.3733	-546.9719	-547.1540	-547.1755	-
I	-622.2894(4.7)	-	-	-623.1930(3.4)	-0.003
II	-622.2943(7.8)	-	-	-	-
III	-622.2894(4.7)	-	-	-	-
IV	-622.2902(5.2)	-	-	-	-
V	-622.2993(10.9)	-622.9974(9.1)	-623.1770(7.5)	-623.1998(7.6)	-0.035
VI	-698.2120(13.5)	-	-	-	-
VII	-698.2236(20.8)	-	-	-699.2212(13.5)	-0.067
VIII	-	-	-	-775.2437(20.0)	-0.061
IX	-	-	-	-851.2560(20.1)	-0.056
X	-	-	-	-927.2703(21.5)	-
Basis Set	A	B	C	D	D

A: 4-31G
B: Double Zeta [S(12s/8p)/<62211/621>, O(9s/5p)/<6111/41>, H(4s)/<31>]
C: Double Zeta + Sulfur d
D: S(12s/8p/1d)/<4s/3p/1d>, O(9s/5p)/<3s/2p>, H(4s)/<2s>

Table 2. Bond distances, bond angles, and dipole moments for fragments and complexes from SCF geometry optimizations

	Basis set	R(SO)	(OSO)	R(OH)	∠(HOH)	∠A ∠B	R_A	Dipole moment
H_2O	A	--	----	0.951	111.2	--	--	2.49
	B	--	----	0.952	112.5	--	--	2.53
SO_2	A	1.530	114.2	---	---	--	--	3.30
	B	1.535	113.0	---	---	--	--	3.44
	C	1.428	118.1	---	---	--	--	2.67
I	A	1.531	113.1	0.951	111.0	--	3.27	--
II	A	1.528/1.534	112.9	0.953/0.949	112.1	--	2.86 2.54	--
III	A	1.525/1.531	114.3	0.953/0.950	110.6	--	2.02	6.10
IV	A	1.531	112.8	0.951	110.3	--	2.37	6.35
V	A	1.533	113.6	0.953	112.5	90.4 124.4	2.48	2.95
	B	1.541	112.6	0.953	113.2	89.4 125.9	2.49	2.92
	C	1.427	115.7	0.953	113.8	87.6 129.0	2.52	2.51
VI	A	1.534	112.5	0.951/0.949	112.3	--	2.85 2.54	--
VII	A	1.541	113.0	0.953	112.5	90.3 124.7	2.48	0.07

All distances are in Angstroms. Dipole moments are in Debyes. A second set of bond lengths is given for asymetric complexes. For the definition of ∠A, ∠B, and R_A see Figure 1.

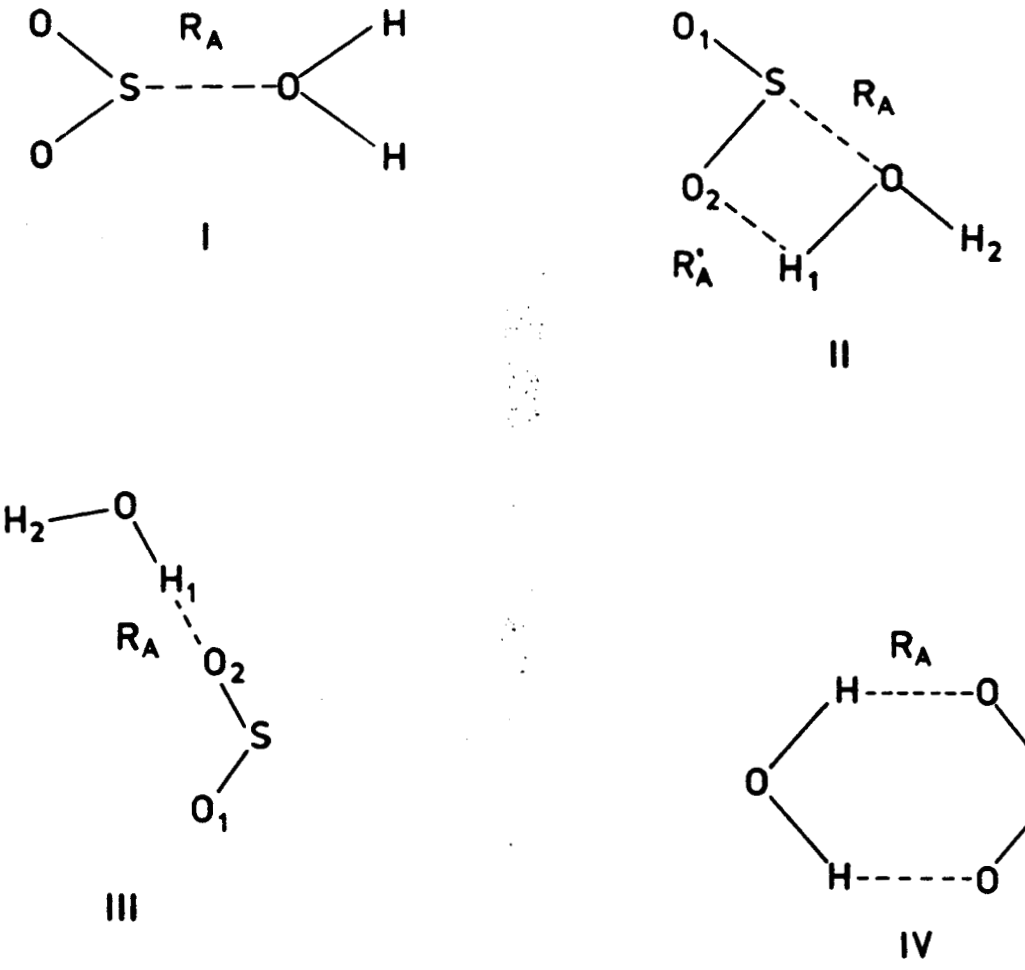
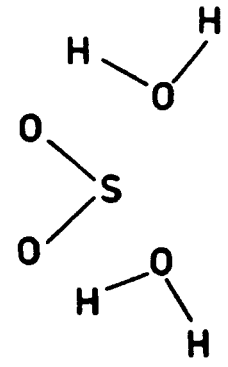


FIGURE 1. CONFORMATIONS OF $SO_2 \cdot H_2O$ COMPLEXES



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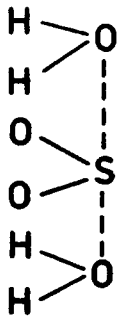

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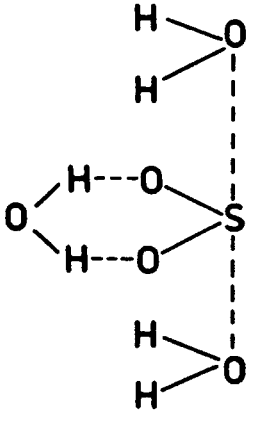

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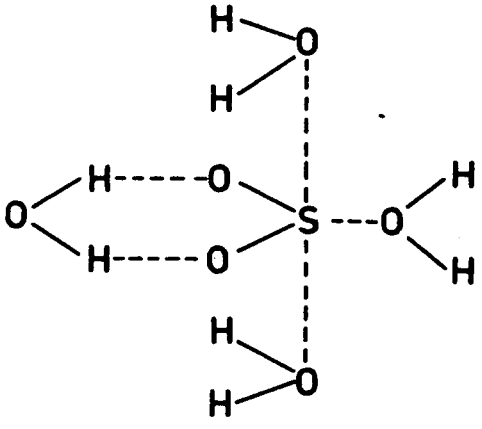

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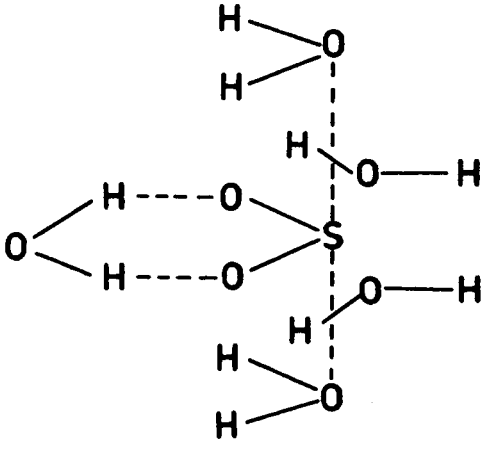

X

FIGURE 2. CONFORMATIONS OF MULTIPLE WATER COMPLEXES OF SO_2.

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